CRYSTAL STRUCTURE OF URALBORITE $Ca_2[B_4O_4(OH)_8]$

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Abstract

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CRYSTAL STRUCTURE OF URALBORITE $Ca_2[B_4O_4(OH)_8]$

The mineral uralborite*—a hydrous calcium metaborate, discovered and described by S. V. Malinko in 1961 (^{1})—was kindly supplied by him to the crystal-chemistry laboratory of the All-Union Institute of Mineral Raw Materials for detailed structural investigation. Careful X-ray study of the specimens supplied established the presence of yet another calcium metaborate—vimsite (^{2}).

The occurrence of vimsite together with uralborite makes it necessary to treat critically the chemical analysis of the latter given in (^{1}). A repeated microchemical analysis of uralborite (T. I. Stolyarova, chemical laboratory of the All-Union Institute of Mineral Raw Materials) made it possible to conclude that the formula of the mineral $CaB_2O_4 \cdot 2H_2O$, previously derived from a complete chemical analysis (wt. %): SiO_2 4.00; Al_2O_3 1.12; Fe_2O_3 2.13; CaO 35.27; MgO 0.67; B_2O_3 38.06; H_2O^+ 19.08; $\Sigma = 100.33\%$, with the ratio $CaO : B_2O_3 : H_2O = 1 : 1 : 2$, is retained, and it was adopted as the basis for a detailed X-ray structural investigation.

The parameters of the monoclinic cell, refined by the powder method (RKU-114), are: $a = 6.92 \pm 0.01$ Å; $b = 12.35 \pm 0.02$ Å; $c = 9.80 \pm 0.02$ Å; $\beta = 83°$. With specific gravity $d = 2.60$ g/cm^3, the cell contains $z = 8$ units of $CaB_2O_4 \cdot 2H_2O$.

The principal experimental material for the structure determination of uralborite was provided by layer-line scans (Weissenberg photographs, Mo radiation) about the axes a, b, and c: $0kl$–$5kl$, $hk0$, $hk1$, $h0l$, $h1l$ ($\max \sin\theta/\lambda = 0.95$ Å^{-1}). Reflection intensities were estimated on the standard $\gamma/2$ scale of blackening standards. Systematic extinctions on the scans unambiguously indicated the space group $C_{2h}^5 = P2_1/n$. The solution of the structure of uralborite, as also of vimsite (^{3}), in accordance with a previously calculated weight criterion ($r' = 1, 2$), was carried out by the heavy-atom method (^{4}).

Table 1

Coordinates of the basis atoms of uralborite

Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
Ca_1	0.698	0.259	0.238	O_8	0.556	0.248	0.729

Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
Ca_2	0.719	0.401	0.864	O_9 (OH)	0.517	0.293	0.039
O_1	0.870	0.072	0.405	O_{10} (OH)	0.729	0.399	0.613
O_2 (OH)	0.585	0.070	0.277	O_{11} (OH)	0.851	0.419	0.076
O_3	0.756	0.097	0.651	O_{12} (OH)	0.639	0.455	0.281
O_4 (OH)	0.576	0.099	0.877	B_1	0.742	0.008	0.338
O_5 (OH)	0.913	0.152	0.067	B_2	0.825	0.153	0.519
O_6 (OH)	0.852	0.220	0.822	B_3	0.682	0.164	0.769
O_7	0.637	0.235	0.484	B_4	0.597	0.308	0.596

A detailed analysis of the Patterson maps $p(uw)$ and $p(vw)$ and the first syntheses of electron density made it possible to localize, in the projections xz and yz, the Ca atoms in general positions. The light O and B atoms were localized from three-dimensional complete and difference syntheses of electron density, constructed from the found coordinates of the Ca atoms.

The resulting structural model was refined by the method of least squares–

* Named after the locality of its discovery in the Urals.

Table 2

Interatomic distances in the structure of uralborite (Å)

B_1 tetrahedron	Distance	**B_2 tetrahedron**	Distance
B_1–O_2(OH)	1.51	B_2–O_3	1.49
B_1–O_1	1.41	B_2–O_7*	1.46
B_1–O_{12}(OH)*	1.50	B_2–O_1	1.50
B_1–O_{11}(OH)*	1.49	B_2–O_9(OH)*	1.52
O_1–O_2(OH)	2.47	O_3–O_7*	2.45
O_1–O_{12}(OH)*	2.39	O_3–O_1	2.46
O_1–O_{11}(OH)*	2.43	O_3–O_9(OH)	2.41
O_2(OH)–O_{11}(OH)*	2.33	O_7*–O_1	2.45
O_2(OH)–O_{12}(OH)*	2.42	O_7*–O_9(OH)	2.43
O_{11}(OH)*–O_{12}(OH)*	2.39	O_1–O_9(OH)	2.42

Mean	Distance	**Mean**	Distance
B_1–O(OH)	1.48	B_2–O(OH)	1.49
O–O(OH)	2.41	O–O(OH)	2.44

B–O–B angles	Angle	**B–O–B angles**	Angle
B_1–O_1–B_2	129°8′	B_2–O_3–B_3	117°10′

B_3 tetrahedron	Distance	**B_4 tetrahedron**	Distance
B_3–O_3	1.47	B_4–O_{10}(OH)	1.47
B_3–O_8	1.44	B_4–O_7*	1.50
B_3–O_6(OH)	1.51	B_4–O_8	1.50
B_3–O_4(OH)	1.46	B_4–O_5(OH)	1.43
O_3–O_8	2.40	O_{10}(OH)–O_7*	2.43
O_3–O_6(OH)	2.42	O_{10}(OH)–O_8	2.42
O_3–O_4(OH)	2.41	O_{10}(OH)–O_5(OH)	2.37
O_8–O_6(OH)	2.37	O_7*–O_8	2.47
O_8–O_4(OH)	2.36	O_7*–O_5(OH)	2.42
O_6(OH)–O_4(OH)	2.43	O_8–O_5(OH)	2.33

Mean	Distance	**Mean**	Distance
B_3–O(OH)	1.47	B_4–O(OH)	1.50
O–O(OH)	2.40	O–O(OH)	2.41

B–O–B angles	Angle	**B–O–B angles**	Angle
B_2–O_7*–B_4	117°30′	B_3–O_8–B_4	122°7′

Ca_1 polyhedron	Distance	**Ca_2 polyhedron**	Distance
Ca_1–O_2(OH)	2.48	Ca_2–O_8	2.64
Ca_1–O_7	2.41	Ca_2–O_6(OH)	2.43
Ca_1–O_9(OH)	2.48	Ca_2–O_{10}(OH)	2.45

Ca_1 polyhedron	Distance	**Ca_2 polyhedron**	Distance
Ca_1–O_5(OH)	2.49	Ca_2–O_3*	2.43
Ca_1–O_{11}(OH)	2.68	Ca_2–O_{11}(OH)	2.38
Ca_1–O_8*	2.47	Ca_2–O_2(OH)	2.59
Ca_1–O_{12}(OH)	2.48	Ca_2–O_1*	2.42
Ca_1–O_6*	2.41	Ca_2–O_9(OH)	2.49
O_2(OH)–O_9(OH)	3.68	O_8–O_6(OH)	2.37**
O_2(OH)–O_6(OH)	3.06	O_8–O_{10}(OH)	2.42**
O_2(OH)–O_7	3.02	O_8–O_9(OH)	3.06
O_2(OH)–O_8	3.94	O_8–O_1	3.01
O_2(OH)–O_5(OH)	3.05	O_6(OH)–O_{10}(OH)	3.20
O_5(OH)–O_8	2.33**	O_6(OH)–O_2(OH)*	3.06
O_5(OH)–O_9(OH)	3.29	O_6(OH)–O_{11}(OH)	3.50
O_5(OH)–O_{11}(OH)	3.33	O_6(OH)–O_9(OH)	3.08
O_{11}(OH)–O_9(OH)	2.85	O_9(OH)–O_{11}(OH)	2.87
O_{11}(OH)–O_8*	3.01	O_9(OH)–O_1*	2.42**
O_{11}(OH)–O_{12}(OH)	2.39**	O_{11}(OH)–O_1*	3.90
O_{12}(OH)–O_7	3.41	O_{11}(OH)–O_2(OH)*	3.17

(continued)

Ca_1 polyhedron	Distance	Ca_2 polyhedron	Distance
O_{12}(OH) –O_8 *	3.81	O_1 * – O_{10}(OH)	3.57
O_{12}(OH) – O_6(OH)	2.90	O_2(OH)* – O_{10}(OH)	3.13
O_{12}(OH) – O_9(OH)	3.29	O_3 * – O_2(OH)*	3.14
O_7 –O_8 *	3.35	O_3 * – O_{10}(OH)	3.38
O_7 –O_6(OH)	2.98	O_3 * –O_1 *	3.31
O_9(OH) – O_6(OH)	2.86	O_3 * – O_{11}(OH)	3.27

Averages	Distance	Averages	Distance
Ca_1 –O(OH)	2.49	Ca_2 –O(OH)	2.48
O –O(OH)	3.15	O –O(OH)	3.21

* Atoms that are related to the corresponding basis atoms by symmetry elements of the group.
** Common edges are shortened in accordance with Pauling' s rule.

tions on the M-20 machine at the Computing Center of Moscow University, using the programs of B. L. Tarnopol' skii and V. I. Andrianov (^{5}). The final coordinates of the basis atoms of uralborite (54 parameters) are given in Table 1. The discrepancy factor corresponding to these coordinates for 1600 independent and nonzero reflections is $R_{hkl} = 15.1\%$ ($B = 0.4$ Å^2).

Interatomic distances are given in Table 2. From them, taking into account the valence balance and the gross chemical formula, it follows that in uralborite, as in vimsite, there are no "whole" H_2O molecules, and in the anionic part O^{2-} and OH^- groups are specifically distinguished.

In the structure of uralborite all boron atoms are in tetrahedral coordination and form a compact island group of four crystallographically independent B-tetrahedra connected by common vertices. As usual, the O atoms common to two adjacent B atoms, while the eight anions participating in the coordination of only one B (and Ca), are represented by OH^- groups, i.e., the formula of the island boron-oxygen radical in uralborite is $[B_4O_4(OH)_8]^{4-}$. As is seen from Fig. 1, in the boron-oxygen radical three B-tetrahedra form a triple ring, similar to the silico-oxygen ring $[Si_3O_9]$, and the fourth is attached to it through a common vertex. This radical may be regarded as the interesting feature of the structure of uralborite that has been revealed, primarily as a previously unknown new radical of tetrahedra; the discovery of this radical changes the position

Fig. 1. Uralborite. Projection *yz*. Oxygen tetrahedra are emphasized; Ca atoms belonging to the cell are shown by spheres.

of uralborite in the classification of borates: contrary to the earlier classification (^{6}, ^{7}), which assigned it to the chain group, it falls into the category of island borates. The addition (external) of a fourth tetrahedron to the triple ring did not change the metacharacter of the radical: $[B_{3+1}O_{12}] = [BO_3]_4$.

Two independent Ca atoms are located in 8-vertex polyhedra in the form of 12-face-

approximately equal in volume. These delta-dodecahedra (all faces are triangles) join along a common edge into pairs which, obeying the glide plane n at two levels, are extended along the long diagonal $(a + c)$ of the (010) projection into an infinite ribbon; neighboring pairs in the ribbon are also connected along common edges. This ribbon is linked by vertices on two sides in the direction

Fig. 2. Uralborite. Layer of Ca polyhedra

Figure 1: Fig. 2. Uralborite. Layer of Ca polyhedra

Fig. 3. Uralborite. Section $x = \frac{1}{4}$. Geometry of the connection of Ca polyhedra by boron-oxygen radicals in the direction of the b axis

Figure 2: Fig. 3. Uralborite. Section $x = \frac{1}{4}$. Geometry of the connection of Ca polyhedra by boron-oxygen radicals in the direction of the b axis

of the diagonal $(a - c)$ with two translationally identical ribbons, forming an infinite layer of Ca polyhedra (Fig. 2). For the period $b = 12.34$ Å there are two such layers at the levels $y = \frac{1}{4}$ and $y = \frac{3}{4}$, constituting the "engineering" basis of the structure. The layers of Ca polyhedra in uralborite resemble layers of Sc octahedra with a corundum motif—six-membered loops in the structure of tortveitite ([8,9]). The boron-oxygen radicals $[B_4O_4(OH)_8]^{4-}$ fit into the six-membered rings of Ca polyhedra, cementing them and joining with them by common edges (in the two stories of Ca polyhedra, by pairs of very shortened edges; Table 2) and common vertices. In the section of the structure perpendicular to the a axis (Fig. 3), the cementation of two layers by B tetrahedra into a three-dimensional framework is clearly visible. The connection of the layers with one another by boron-oxygen groups is so strong that, despite the layered arrangement of the Ca polyhedra, cleavage is absent in the mineral. In accordance with the structure determined, the formula of the mineral is $Ca_2[B_4O_4(OH)_8]$.

Fig. 2. Uralborite. Layer of Ca polyhedra

Fig. 3. Uralborite. Section $x = \frac{1}{4}$. Geometry of the connection of Ca polyhedra by boron-oxygen radicals in the direction of the b axis

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Note: Figure translations are in progress. See original paper for figures.